1,095,959

PATENT SPECIFICATION

NO DRAWINGS

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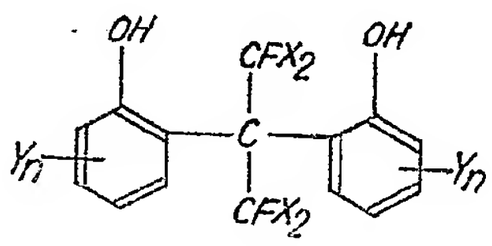
COMPLETE SPECIFICATION

Di-(Fluoromethyl)-Methylene Bisphenols

We, STECKER INTERNATIONAL S.P.A., a body corporate organized and existing under the laws of Italy, of Via Turati No. 29, Milano, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to methylene bisphenol compounds, wherein the methylene group has two methyl substituents, each of which contains at least one fluorine atom. More specifically, it deals with compounds having the following general formula:



where X is bromine, chlorine, iodine or fluorine,

Y is methyl, bromine, chlorine, iodine or fluorine, and

n is a numeral from 0 to 3.

It has been found that superior biochemical and solubility characteristics can be obtained in 2,2′-methylene bisphenols by attaching, to the methylene groups, two halo-substituted methyl groups, having at least one fluorine atom apiece. Such methyl groups may be fluoro-dichloromethyl, difluorochloromethyl or trifluoromethyl. Excellent germicidal properties are obtained with such compounds, as are apparent from the data given in Table I. The marked effectiveness of the germicidal properties of the compounds of the present invention is readily perceived. For example, Compound 9 has an effectiveness of 15.0 against *Staph. aureus*, whereas the corresponding tetrabromo bisphenol containing an unfluorinated bridge shows a zone of inhibition of only 2.0 mm. The compounds also have anthelmintic and other valuable properties.

The compounds of the present invention may be prepared as follows:

PREPARATION

About 0.1 mole of a halogenated acetone is added to a mixture of 0.09 mole of phenol and 0.15 mole of anhydrous hydrogen fluoride, while being cooled with dry ice. The reactants then are sealed in a glass ampoule and heated on a steam bath for 10 hours, after which the contents are poured into a copper vessel. The unreacted phenol is steam-distilled after the evaporation of the hydrogen fluoride, and the residue is recrystallized from ethylene chloride. The yields of products are relatively high, falling in the range of 75% to 95% theory.

Since the halogenated acetone forms the methylene bridge, the type of methyl substituents can be determined by selecting the proper halogens in the acetone. Also, the phenol is substituted with the desired substituents prior to the condensation, although halogenation of the condensation product also is possible.

Table I identifies various compounds of the invention prepared as described above from a suitable halogenated acetone and a phenol carrying the required substituents, and shows their germicidal effectiveness when tested against *Staphylococcus aureus*.

The effectivity of each compound tested was determined by the standard "Zone of Inhibition" test as described for example in our British Specification No. 996,074 at Example 1.

In determining the activity of the compounds against *A. niger*, agar plates were prepared with concentrations of the compounds ranging from 1 p.p.m. to 10 p.p.m., utilizing 20 plates for each compound. The plates containing the lowest concentration of compound which inhibited fungal growth for

[*Price 4s. 6d.*]

14 days at room temperature were considered as the end-point and, in cases where growth was doubtful between one concentration and the next higher, the reading was assumed to fall between such concentrations. When tested thus, all compounds of the invention used were found to be effective against *Aspergillus niger*.

These compounds have been found to be excellent mildew-proofing and germicidal agents for fibrous materials such as cloth, leather, paper, wood, and the like. Treatment of fibrous material may be made with a solution or dispersion of the germicide in a liquid medium, leaving about 0.001% to 5.0% by weight of the germicide in the fibrous material.

The germicides of the present invention also may be incorporated in rubber and synthetic polymers, e.g. polyethylene, polystyrene, polyurethane, nylon, and similar plastoform and elastoform compositions by incorporating the germicide in an amount of 0.001% to 5.0% in the batch which is mixed or kneaded prior to vulcanization, extrusion or other forming operation.

The compounds of the present invention are particularly valuable in detergent and toilet detergent compositions, in the amount of 0.001% to 10%. They may be admixed in commercial toilet soaps, such as neutral high grade sodium and potassium salts of fatty acids from tallow, olive oil, palm oil, and the like, above or with non-soap synthetic detergents, e.g. nonionic, anionic, or cationic.

The term "detergent" employed herein includes fatty acid soaps, as well as synthetic detergents, and other detergents, such as fatty alcohol sulfates, fatty acid amides, sodium tripolyphosphates, and combinations thereof. The term "toilet soap" used herein also is employed in its popular meaning, that is, those compositions employed for cleansing the skin and prepared from an alkali metal compound, such as potassium or sodium hydroxide and fat or fatty acid, both saturated and unsaturated. The compositions described herein also include other antiseptic agents, emollients, water softeners, antioxidants, dyes, perfume, "cold cream" additives, and the like.

TABLE I

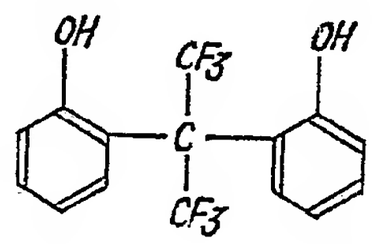
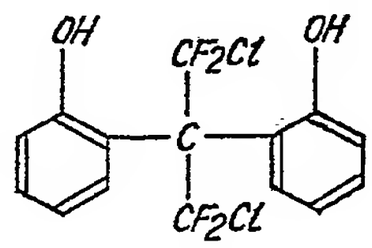
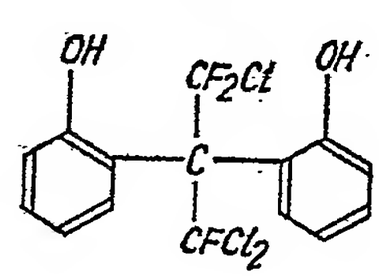
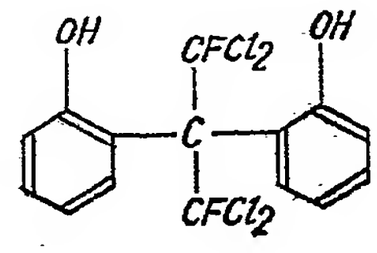
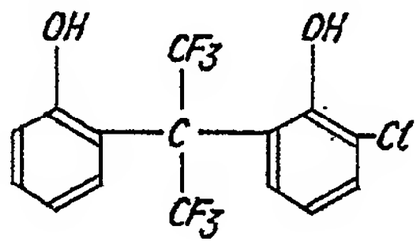
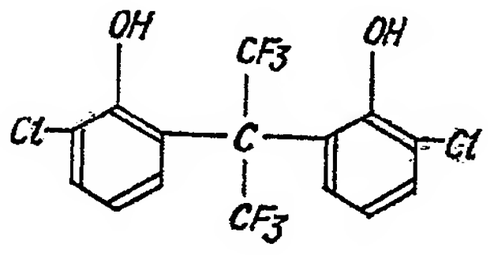
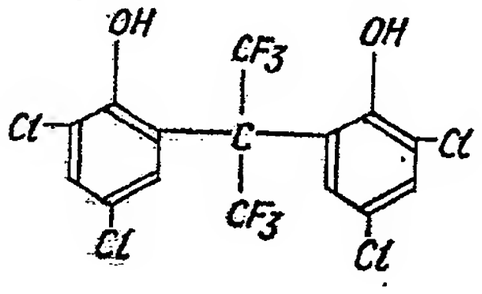
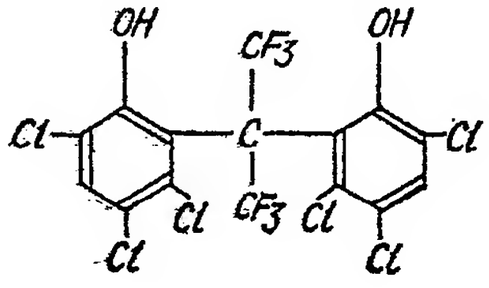
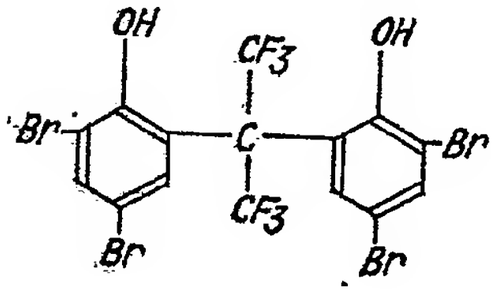
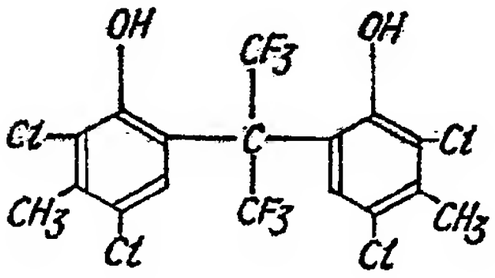
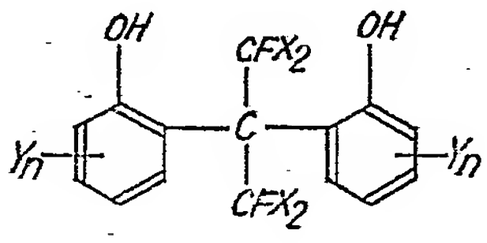
Compound No.	Formula	Zone of Inhibition mm.
1.		8.0
2.		10.0
3.		10.0
4.		10.0

TABLE I—Continued

Compound No.	Formula	Zone of Inhibition mm.
5.		9.0
6.		10.0
7.		14.0
8.		14.0
9.		15.0
10.		11.0

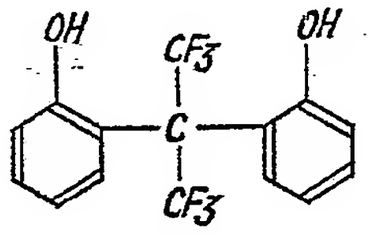
WHAT WE CLAIM IS:—

1. The compounds of the general formula:—

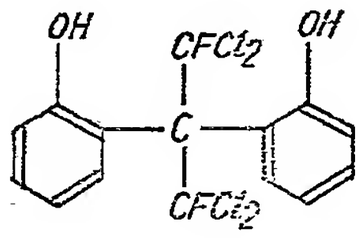


wherein X is bromine, chlorine, iodine or fluorine,
Y is a methyl, bromine, iodine, chlorine or fluorine, and
n is a numeral from 0 to 3.

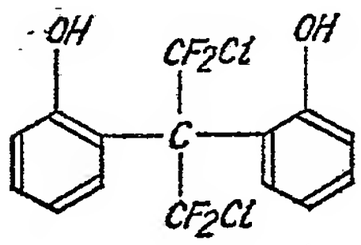
2. The compound of formula:—



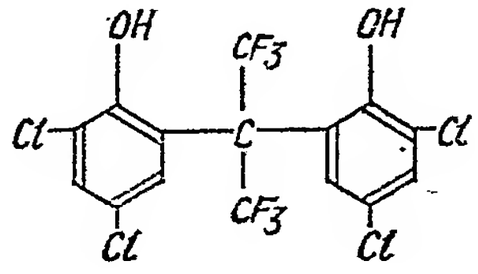
3. The compound of formula:—



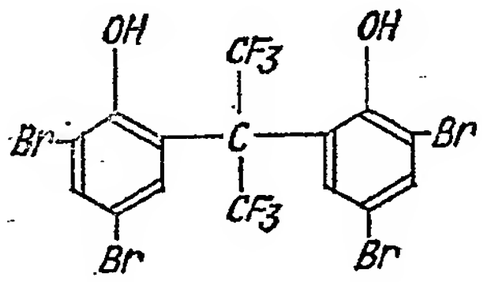
4. The compound of formula:—



5. The compound of formula:—



6. The compound of formula:—



7. Compositions comprising at least one compound according to any one of the preceding claims together with a soap and/or detergent.

8. Compositions comprising at least one compound according to any one of claims 1 to 6 together with a synthetic polymer and/or rubber.

9. Fibrous materials whenever impregnated with at least one compound according to any one of claims 1 to 6.

10. Compositions according to claim 7 wherein the total weight of said compounds is in the range 0.001% to 10% of the total weight of the composition.

11. Compositions according to claim 8 wherein the total weight of said compounds is in the range 0.001% to 5% of the total weight of the composition.

12. Fibrous materials according to claim 9 wherein the total weight of said compounds is in the range 0.001% to 5% of the total weight of said impregnated materials.

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